

## THE FORMATION OF BTX BY THE HYDROPYROLYSIS OF COALS

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### ABSTRACT

The pyrolysis of British coals has been studied at hydrogen pressures of 50 to 150 bar in single- and two-stage, tube reactors at heating rates of up to  $30 \text{ K s}^{-1}$ . In the single stage reactor, hydrolypyrolysis of a high-volatile coal gave up to 4.5% single-ring aromatics; the results suggested that the evolution of volatiles and their cracking to benzene were sequential reactions. This was confirmed using a two-stage reactor in which the coal was heated at a controlled rate and the volatiles cracked in a separate zone at constant temperature. Yields of up to 12% benzene were obtained from a high volatile coal in hydrogen (similar to the yields obtained by various workers from American coals by flash pyrolysis) without very rapid heating of the coal. Hydropyrolysis of model compounds showed that benzene was a major product of the cracking of polynuclear aromatics under hydrogen pressure.

### 1. INTRODUCTION

The carbonisation of coal under hydrogen pressure is known as 'hydro-pyrolysis'. A review of published work<sup>1</sup> showed that flash hydropyrolysis of coal, which involves heating rates of hundreds of  $\text{K s}^{-1}$ , can give appreciable yields of light aromatic hydrocarbons such as benzene, toluene and xylenes (BTX). The present paper is concerned with studies of both single-stage and two-stage hydropyrolysis of coals aimed at producing single-ring aromatics, especially benzene, from coal. In the single-stage reactor the carbonisation and cracking zones are heated by the same source, while in the two-stage reactor there is independent control of the carbonisation and cracking zones.

### 2. MATERIALS

#### 2.1. Coals

The analyses of the coals used for hydropyrolysis are given in Table 1. The coals were ground, sized +251 -500  $\mu\text{m}$  and dried at 373 K in vacuum.

#### 2.2. Model Compounds

Hydropyrolysis experiments were also carried out on six aromatic hydrocarbons: benzene, toluene, p-xylene, naphthalene, anthracene and phenanthrene. Where possible, 'ANALAR' grade chemicals were used without further purification. As the hydropyrolysis reactor was only suitable for solids, 1g of compound was either absorbed on or mixed with 9g of active carbon (NCB Anthrasorb).

### 3. SINGLE-STAGE HYDROPYROLYSIS

#### 3.1. Experimental

The design of the reactor is based on that used by Hiteshue and co-workers at the USBM<sup>2</sup>. A 1830 mm long x 8 mm ID stainless steel, pressure tube in which about 10g of coal were secured between degreased wire wool plugs was heated by passing a large current (up to 1600A) through its wall. The heating rate was controlled by switching tappings on a transformer. The pyrolysis

vapours were swept out of the reaction zone by pressurised hydrogen at up to 150 bar, some of the liquid products collecting in the ice-cooled trap. The remaining liquid products and gases were reduced to atmospheric pressure through a needle valve, which was also used to control the flow rate, before being collected for analysis. The products in the trap were weighed and then washed from the trap and adjoining tubing with chloroform. The residual char in the reactor was weighed and analysed.

### 3.2. Product Analysis

Both gaseous and liquid products were analysed by chromatography. The hydrocarbon gases were measured on an alumina column with a flame ionisation detector, and the permanent gases on a molecular sieve 5A column with a katharometer detector. The liquids were measured using a silicone SCOT column with a flame ionisation detector. Water was estimated by titration with Karl Fisher reagent. Proximate and ultimate analyses were carried out on selected char samples.

### 3.3. Results

The effect of variations in the final heat-treatment temperature and in the vapour residence time on the yields of single-ring aromatics formed by hydropyrolysis of high-volatile Linby coal was investigated using heating rates in the range 7 to 30 K s<sup>-1</sup>, a pressure of 150 bar and zero solids residence time at maximum temperature.

#### 3.3.1 The effect of final heat-treatment temperature

The effect of the final carbonisation temperature on the yields of benzene, toluene and xylenes (BTX) and phenol, cresols and xylenols (PCX) is shown in Figure 1, where it can be seen that for a vapour residence time of approximately 10 s the yields of both BTX and PCX passed through a maximum at a temperature of about 1000 K. The maximum yield of single-ring aromatics was approximately 4.5%, being composed of about equivalent amounts of BTX and phenolics.

#### 3.3.2 The effect of vapour residence time

The effect of vapour residence on the yields of BTX and PCX at heating rates of 10, 20 and 30 K s<sup>-1</sup> to a final heat-treatment temperature of 1000 K is shown in Figures 2a and b. The yield of BTX increased steadily over the range of residence times investigated and was little affected by the heating rate. In contrast, the yield of PCX passed through a maximum at a residence time of 3 s and was markedly affected by the heating rate, at the two higher heating rates the PCX being almost completely destroyed after 8 s. Dehydroxylation of the PCX to BTX at the longer residence times only partly explains the fate of the PCX since the decrease in PCX is considerably greater than the increase in BTX.

## 4. TWO-STAGE HYDROPYROLYSIS

### 4.1 Modification to Apparatus

The modification to the hydropyrolysis apparatus to enable the carbonisation and cracking zones to be separated is shown in Figure 3. The upper portion of the stainless steel tube reactor, which served as the cracking zone, was thermostatically controlled at temperatures up to 1273 K using two muffle furnaces; the lower portion which contained the coal was electrically heated as previously.

## 4.2 Experimental

The samples (coals, coking coals plus coke and model compounds on active carbon) to be pyrolysed were placed, as before, in the lower section of the tube. The flow of hydrogen through the reactor was established to give the required vapour residence time with the upper section maintained at the cracking temperature. Current was then passed through the lower section to heat it and the sample to the carbonisation temperature. The products were collected and analysed in the same way as with the single-stage reactor.

## 4.3. Results

### 4.3.1 Effect of carbonisation time, temperature and heating rate

The effect of varying the carbonisation time is shown in Figure 4. The methane increases monotonically with time and the benzene yield reaches a limit of about 11% w/w on d.a.f. coal at 9 minutes. Thus, to achieve optimum benzene yield with minimum methane formation, the residence time of the coal should be controlled.

Varying the final carbonisation temperature from 848 to 973 K (at a carbonisation time of 9 minutes) while cracking the products at 1123 K gave the results plotted in Figure 5. Methane increases monotonically with increase in final carbonisation temperature whereas ethane and benzene pass through broad maxima at about 923 K, the benzene yield peaking at 12% w/w on d.a.f. coal (13.4% C on C). The lower benzene yield at 973 K suggests that, at this temperature, some of the benzene is destroyed during the carbonisation stage. The volatile matter content of the char decreased from about 16% at a carbonisation temperature of 750 K to 5.5% at 923 K.

The results of tests on the effect of heating rate show that, at a carbonisation temperature of 750 K, increasing the heating rate of the coal from 1 to 25 K s<sup>-1</sup> has no significant effect on benzene yields, although the methane and ethane yields are reduced by the higher heating rate.

### 4.3.2 Effect of cracking temperature and residence time

The yields of gases and liquids were determined after cracking at temperatures from 773 to 1223 K using the relatively low carbonisation temperature of 750 K and a carbonisation time of 15 minutes.

The yields of methane, ethane, benzene and tar are given in Figure 6. Above 900 K, increasingly severe cracking of the carbonisation vapours gives continuously increasing yields of methane, whereas the ethane and benzene pass through broad maxima. The yield of tar decreases with increasing temperature, suggesting that tar vapours are the precursors of much of the ethane and benzene, themselves being hydrogenated to methane under more extreme conditions.

The effect of varying the hydrogen flow rate and hence the gaseous residence time was also investigated. The carbonisation temperature was 873 K and the pressure was 150 bar. The results are summarised in Figure 7 and show that, as the hydrogen flow was increased, the yields of ethane and benzene increased and the benzene passed through a broad maximum. At the lower hydrogen rates, the volatiles were overcracked to give high methane yields. The lowest hydrogen rate of 0.85g min<sup>-1</sup> (equivalent to a flow of 0.01 m<sup>3</sup> min<sup>-1</sup> at room temperature and pressure) gave a gaseous residence time of about 7 s in the cracking zone at 150 bar and 1123 K.

#### 4.3.3 Effect of pressure

Tests at 50, 100 and 150 bar in which the vapour residence time was maintained constant by using a constant linear hydrogen velocity gave the results shown in Figure 8. Methane and ethane yields increased linearly with pressure but the benzene yield increased less than proportionally to pressure.

#### 4.3.4 Effect of coal-rank

The results on the effect of coal-rank are summarised as yields versus carbon content of coal in Figure 9 and suggest that the maximum ethane and benzene yields are obtained from the CRC 800 coals. Anthracite, as expected, gave less volatile hydrocarbons, and the coking coals tended to cake in the carboniser and would therefore be difficult to process continuously. The high volatile brown coal contained 24.8% oxygen and the oxygen appeared mainly as water rather than carbon oxides. The Lady Victoria coal gave comparatively low benzene and high methane yields, probably reflecting the high aliphatic content of this coal.

#### 4.3.5 Model compounds

Table 2 gives the results of the hydropyrolysis of the aromatic compounds listed in Section 2.2.; only the aromatic products are listed. The cracking temperature was varied from 823 to 1173 K at a constant vapour residence time of about 5 s. As might be expected, the extent of decomposition increased with increasing temperature, and the percentage remaining undecomposed at 973 K was taken as a measure of thermal stability. The stability sequence in order of decreasing stability was as follows: benzene = naphthalene > phenanthrene > p-xylene > anthracene. It should however be stressed that the order depends on the temperature. Thus, at 1073 K toluene and p-xylene are less stable than anthracene.

The yield of benzene at three temperatures (973, 1073, 1173 K) from the model compounds is shown as a bar chart in Figure 10. Benzene survives both as a feedstock and as a product of the cracking of toluene, p-xylene and polynuclear hydrocarbons. It is interesting that naphthalene, anthracene and phenanthrene give benzene as a major product at the two higher cracking temperatures.

### 5. DISCUSSION

In line with the various groups of American workers<sup>2-5</sup> who have studied hydropyrolysis, the carbonisation of coal under hydrogen pressure has been shown to give much higher yields of light aromatics, in particular benzene, than are obtained by conventional carbonisation, i.e. at atmospheric pressure in an inert atmosphere.

The results of the experiments carried out in a single-stage reactor similar to that used by Hiteshue, Anderson and Schlesinger<sup>2</sup> are in good agreement with their published data. With this apparatus which employs relatively slow heating rates (up to  $30 \text{ K s}^{-1}$ ) a maximum yield of 4.5% single-ring aromatics can be expected from a low-rank coal.

In these single-stage reactors the temperature cycle of the reactor together with the hydrogen flow rate through it determine the conditions for both the pyrolysis of coal and the hydrocracking of the volatiles produced. Thus, it is impossible to optimise simultaneously both the carbonising and cracking conditions. However, in the two-stage hydropyrolysis reactor, the carbonisation and cracking processes have to a large extent been separated and it is therefore possible to optimise separately the conditions for each.

The present work with the two-stage reactor shows that yields of over 10% benzene can be obtained from a low-rank coal without the need for heating at very high rates (up to  $1000 \text{ K s}^{-1}$ ). From the point of view of the design of a hydropyrolysis plant, a process employing a moderate heating rate should be preferable since it is likely to be difficult to achieve very fast heating on an industrial scale.

## 6. CONCLUSIONS

The present study has:

- (i) confirmed that hydropyrolysis of coal produces appreciable yields of single-ring aromatics, especially benzene, and has shown that a benzene yield in excess of 10% can be obtained without heating the coal very rapidly;
- (ii) shown that the benzene yield depends on the temperature of the cracking zone and the residence times of the volatiles in this zone;
- (iii) demonstrated the potential of a two-stage reactor whereby the pyrolysis and cracking stages can be independently controlled, and which should make it simpler to optimise the yields of desired products.

## 7. ACKNOWLEDGMENTS

We thank the National Coal Board for permission to publish this paper and the European Coal and Steel Community for financial support. The views expressed are those of the authors and not necessarily those of the National Coal Board.

## 8. REFERENCES

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Table 1: Analyses of Coals

Colliery or Coal Type	NCB CRC No.	Grade	Proximate analysis			Ultimate analysis					Maceral analysis % v/v			Coking Test		
			Moisture a.r.	Ash d.b.	V.M. d.a.f.	C	H	N	O	Total Cl S	Vitrinite	Exinite	Inertinite	Gray King Coke Type	Swelling No.	
d.m.m.f.					a.r.											
Coed Bach	101	Washed duff	2.5	5.6	5.7	93.9	3.1	1.25	0.9	0.8	0.08	62	0	38	A	0
Garw	203	Washed smalls	0.8	10.1	17.9	91.6	4.7	1.55	1.6	0.8	0.01	71	Tr.	29	F	7
Pervent-haugh	301b	Washed smalls	0.5	5.3	29.7	87.6	5.5	1.75	4.3	0.8	0.04	N.D.	N.D.	N.D.	G <sub>9</sub>	8½
Bersham	402	Washed + 2 in.	1.9	2.0	38.3	85.9	5.6	1.75	6.8	1.0	0.39	87	3	10	G <sub>9</sub>	8½
Annesley	602	Washed doubles	4.5	2.4	38.6	84.3	5.5	1.9	7.2	0.8	0.49	73	9	18	G <sub>4</sub>	6½
Linby	802	Washed doubles	8.3	5.8	39.1	82.4	5.3	1.95	9.0	1.0	0.46	79	6	15	C	1
Daw Hill	802	Smalls	9.3	11.7	39.7	80.6	4.9	1.4	11.9	1.65	0.23	63	11	26	C	1
Cotgrave	902	Blend A	8.5	14.2	41.5	82.5	5.7	1.85	9.2	0.65	0.26	N.D.	N.D.	N.D.	A	½
Lady Victoria	-	Cannel	2.0	2.9	52.2	84.4	6.8	1.5	5.8	1.3	0.19	26	21	53	E	1
German brown	-	-	13.5	7.6	52.8	69.7	4.6	0.9	24.8	0.25	0.03	N.D.	N.D.	N.D.	A	0

N.D. = Not determined.

Table 2: Yields of Aromatics from Two-stage Hydropyrolysis  
of Aromatics

Feedstock	Cracking Tempera- ture, K	Calc. vapour resi- dence time,s	Yield % w/w on feed					
			Ben- zene	Tol- uene	Xylenes	Naphth- alene	Anthra- cene	Phenan- threne
Benzene	973	5.2	92					
	1023	4.9	101					
	1073	4.6	95					
	1123	4.4	71					
	1173	4.3	18					
Toluene	823	6.1	20	66				
	873	5.7	21	42				
	973	5.2	59	32				
	1023	4.9	54	1				
	1073	4.6	73	0				
	1123	4.4	61	0				
p-xylene	773	6.5	4	21	97			
	873	5.7	4	6	76			
	973	5.2	14	23	21			
	1023	4.9	56	7	8			
	1073	4.6	67	0	0			
Naphtha- lene	773	6.5	1	0.2	0	99		
	973	5.2	4	0.8	0	93		
	1023	4.9	5	2	0	80		
	1073	4.6	24	1	0	52		
	1123	4.4	41	0.4	0	8		
	1173	4.3	23	0.3	0	0.2		
Anthra- cene	773	6.5	0.5	0.4	0	3	16	
	873	5.5	0.5	0.4	0	2	14	
	973	5.2	2	0.7	0	8	9	
	1073	4.6	15	0.4	0	20	7	
	1173	4.3	16	0.1	0	0.6	2	
Phenan- threne	773	6.5	0.4	0	0	0	0	37
	873	5.7	0.5	0	0	0	0	36
	973	5.2	0.9	0	0	0.9	0	42
	1073	4.6	4	0.1	0	2	0	18
	1173	4.3	21	0	0	0.1	0	0.7

Condition: 1g of feedstock with 9g of active carbon  
Carbonised at 750K with 15 min. solids residence time  
Heating rate  $1\text{ K s}^{-1}$   
8 mm ID carboniser and cracker  
Hydrogen  $0.85\text{ g min}^{-1}$  at 100 bar.

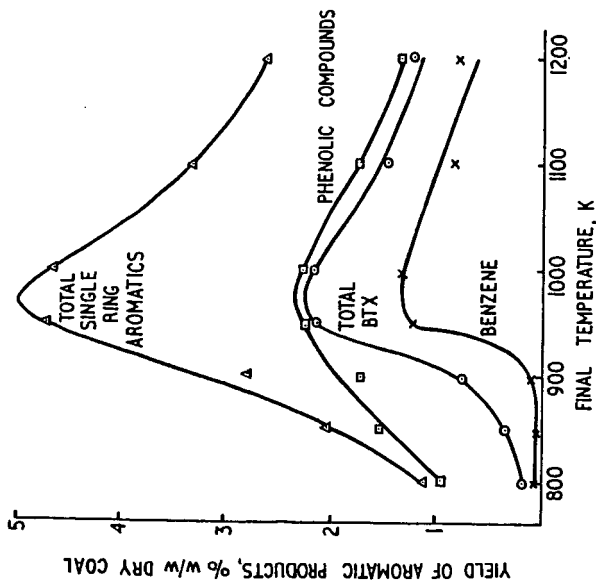


FIGURE 1. EFFECT OF FINAL TEMPERATURE ON YIELD OF PRODUCTS

HEATING RATE  $7\text{Ks}^{-1}$ , PRESSURE 150 BAR, SOLIDS RESIDENCE TIME  $0\text{s}$ , VAPOUR RESIDENCE TIME 11.5, 10 g OF 251 TO 500  $\mu\text{m}$  LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.

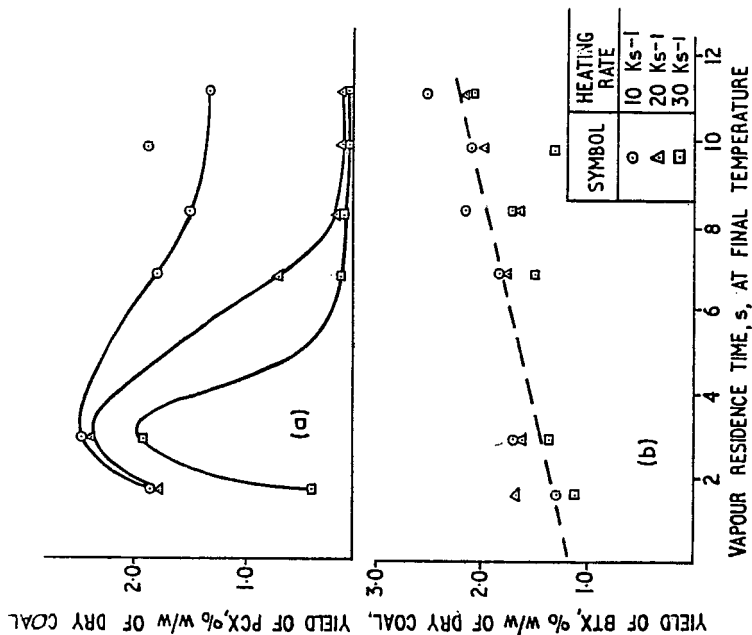


FIGURE 2. EFFECT OF VAPOUR RESIDENCE TIME AND HEATING RATE

ON YIELDS OF (a) PHENOL, CRESOLS AND XYLENOLS (PCX) AND (b) BENZENE, TOLUENE AND XYLENES (BTX)

FINAL TEMPERATURE 1000K, HEATING RATE  $7\text{Ks}^{-1}$  PRESSURE 150BAR, SOLIDS RESIDENCE TIME  $0\text{s}$ , 10g 251 TO 500 $\mu\text{m}$  LINBY COAL, 8mm ID SINGLE-STAGE REACTOR.



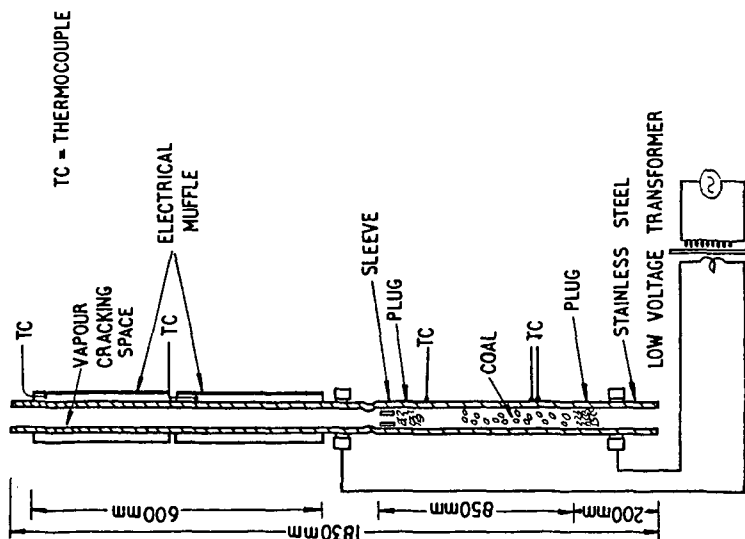


FIGURE 3. DETAILS OF C.R.E. TWO-STAGE REACTOR WITH TEMPERATURE CONTROL OF VAPOUR SPACE

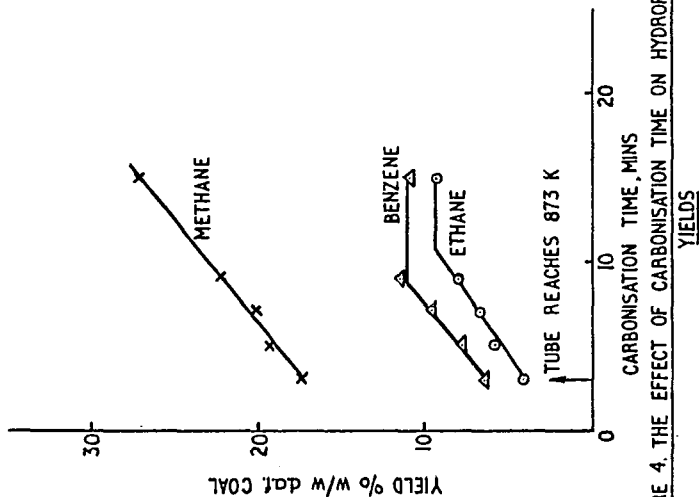


FIGURE 4. THE EFFECT OF CARBONISATION TIME ON HYDROLYSIS

CONDITIONS: HEATING RATE  $5\text{Ks}^{-1}$ , CARBONISATION TEMPERATURE  $873\text{K}$ , CRACKING TEMPERATURE  $1123\text{K}$ , HYDROGEN  $1.44\text{g min}^{-1}$ , PRESSURE  $150\text{ BAR}$ ,  $10\text{g LINBY COAL } 251\text{ TO } 500\mu\text{m}$ ,  $8\text{mm ID CARBONISER AND CRACKER}$ .

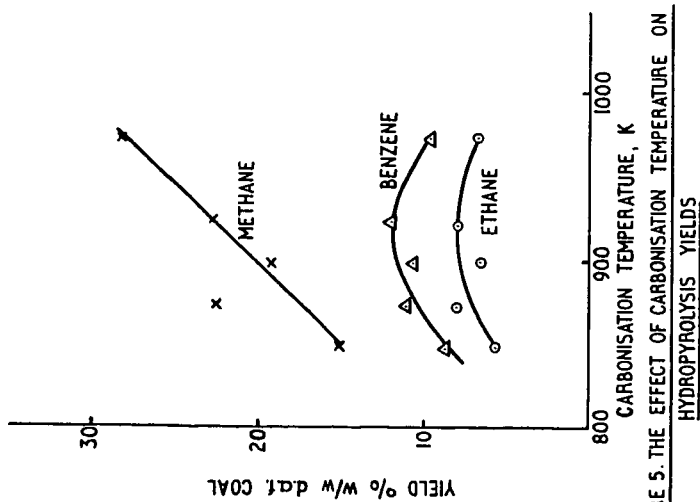


FIGURE 5. THE EFFECT OF CARBONISATION TEMPERATURE ON HYDROLYSIS YIELDS  
 CONDITIONS: HEATING RATE  $5\text{Ks}^{-1}$ , CARBONISATION TIME 9 min, CRACKING TEMPERATURE  $1123\text{K}$ , HYDROGEN  $1.44\text{g min}^{-1}$ , PRESSURE  $150\text{BAR}$ ,  $10\text{g}$  LINBY COAL  $8\text{mm ID}$  CARBONISER AND CRACKER.

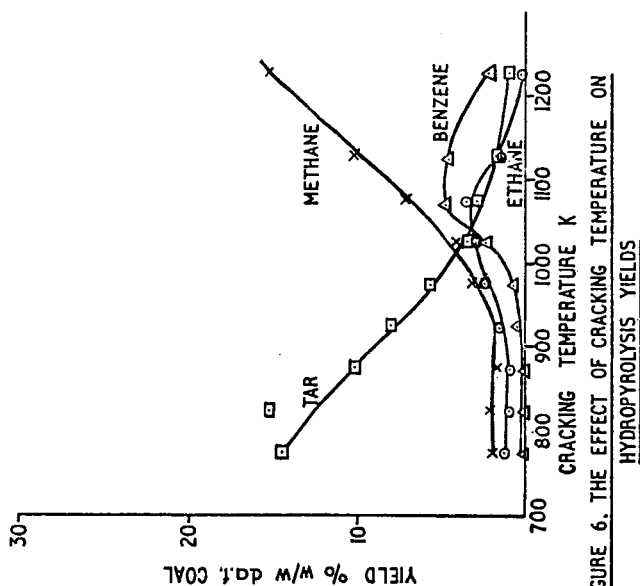


FIGURE 6. THE EFFECT OF CRACKING TEMPERATURE ON HYDROLYSIS YIELDS  
 CONDITIONS: HEATING RATE  $1\text{Ks}^{-1}$ , FINAL CARBONISATION TEMPERATURE  $750\text{K}$ , CARBONISATION TIME 15 min, HYDROGEN RATE  $0.85\text{g min}^{-1}$ , PRESSURE  $100\text{BAR}$ ,  $10\text{g}$  OF  $251\text{ TO }500\mu\text{m}$  LINBY COAL,  $8\text{mm ID}$  CARBONISER AND CRACKER.

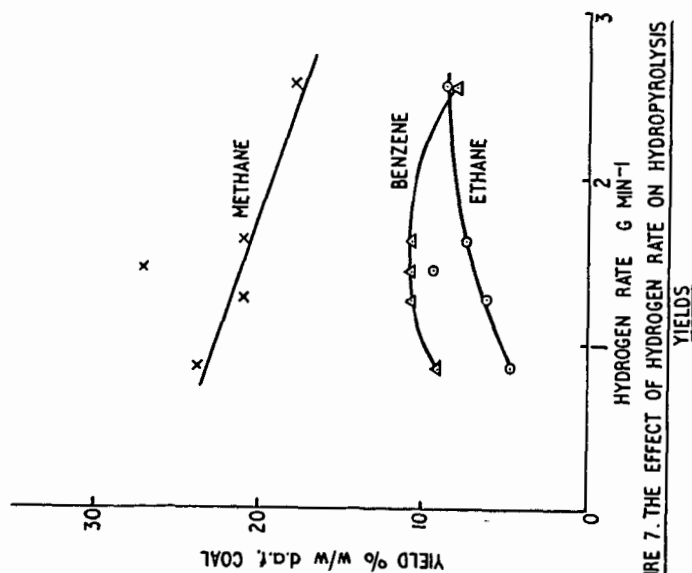


FIGURE 7. THE EFFECT OF HYDROGEN RATE ON HYDROLYSIS YIELDS

CONDITIONS: HEATING RATE  $5\text{Ks}^{-1}$  FINAL CARBONISATION TEMPERATURE  $873\text{K}$ , CARBONISATION TIME  $15\text{min}$ , CRACKING TEMPERATURE  $1123\text{K}$ , PRESSURE  $150\text{BAR}$ ,  $10\text{g}$  OF  $251$  TO  $500\mu\text{m}$  LINBY COAL,  $8\text{mm}$  ID CARBONISER AND CRACKER.

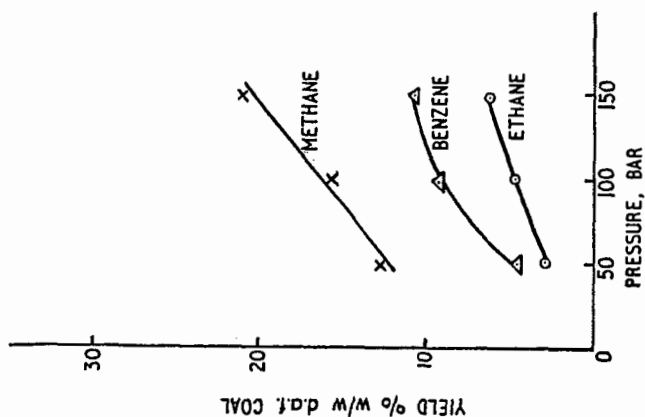


FIGURE 8. THE EFFECT OF PRESSURE ON HYDROLYSIS YIELDS

CONDITIONS: HEATING RATE  $5\text{Ks}^{-1}$ , CARBONISATION TEMPERATURE  $873\text{K}$ , CARBONISATION TIME  $15\text{min}$ , CRACKING TEMPERATURE  $1123\text{K}$ ,  $10\text{g}$  OF  $251$  TO  $500\mu\text{m}$  LINBY COAL,  $8\text{mm}$  ID CARBONISER AND CRACKER.

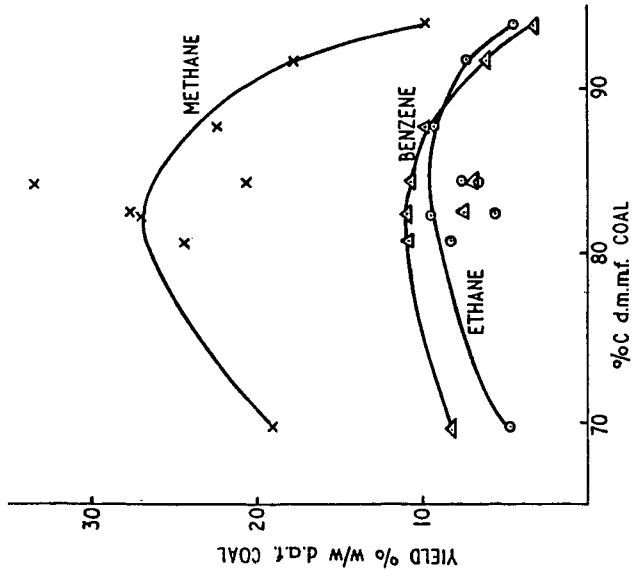


FIGURE 9. THE EFFECT OF COAL RANK ON HYDROPYROLYSIS YIELDS  
 CONDITIONS: HEATING RATE  $5\text{Ks}^{-1}$ , FINAL CARBONISATION TEMPERATURE  
 873K, CARBONISATION TIME 15min, CRACKING TEMPERATURE 1123K,  
 HYDROGEN  $1.44\text{g min}^{-1}$ , PRESSURE 150 BAR, 10g FEEDSTOCK, 8mm ID  
 CARBONISER AND CRACKER.

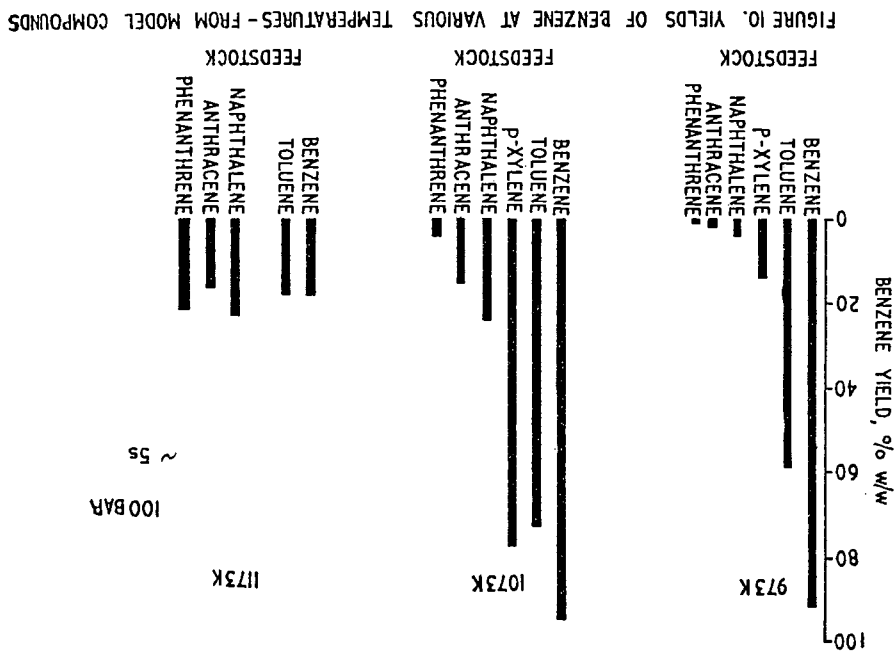


FIGURE 10. YIELDS OF BENZENE AT VARIOUS TEMPERATURES - FROM MODEL COMPOUNDS